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(54) Title: FLUOROPOLYMER COMPOSITIONS, OPTICAL DEVICES, AND METHODS FOR FABRICATING OPTICAL DEVICES

(57) Abstract: Optical waveguides interconnect optical information processing devices, or connect such devices with other optical communication links such as glass optical fibers. Fluoropolymers consisting of alternating perfluorocyclobutane and aryl ether linkages possess suitable properties for optical waveguides and other devices due to tunability in optical properties of the copolymers. Perfluorocyclobutane (PFCB) copolymer may be employed in solutions that exhibit a high solids content. Such solutions show useful physical properties for optical waveguide devices since the solutions are capable of achieving single step film thicknesses, when applied to a substrate, of greater than about 0.6 microns, and sometimes may achieve a thickness of 10 microns or more.

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Title of the Invention

5 Fluoropolymer Compositions, Optical Devices, and Methods for
 Fabricating Optical Devices

Cross Reference to Related Applications

10 This application is related to U.S. Serial No. 09/604,748, which is a regular U.S.
 utility patent application filed 27 June 2000.

Field of the Invention

 This invention relates to the use of fluoropolymers and methods of applying
 fluoropolymers in making components for optical applications. In particular, the
15 invention relates to perfluorocyclobutyl-based compositions.

Background of the Invention

 Optical waveguides interconnect optical information processing devices, or
 connect such devices with other optical communication links such as glass optical
 fibers. Waveguides may be used to create passive optical devices such as splitters,
20 combiners, couplers, routers and the like. In commonly used planar applications,
 waveguides are densely packed on substrates.

 An optical waveguide typically comprises a transparent core that is capable of
 directing light signals therethrough, and a cladding comprising a material that affords a
 lower refractive index than the core material. Waveguides may be constructed as single
25 monolithic structures lithographically provided on a substrate, or may comprise optical
 fibers.

 In the electronics and optical fabrication technologies, optical
 interconnects have been used in backplane interconnections, board-to-board
 interconnections, clock distribution, and a variety of other applications. In particular,
30 lithographic processes have been used because such processes are generally suitable for
 mass production.

 The integration of polymeric materials in optics is an increasingly attractive
 alternative in devices such as switches, optical interconnects, splitters, and surface relief
 structures. As demand for band width and low cost integration has increased, polymers

provide flexibility, high transparency and versatility in structure, and properties. In particular, fluoropolymers represent alternatives to current optical polymers due to their properties, such as low transmission loss (at 1300 and 1550 nm), low birefringence, good optical stability after thermal aging, and low moisture absorption. For example, 5 fluoroacrylates developed by Allied Signal and others, Dupont's Teflon™ AF (tetrafluoroethylene and perfluorovinyl ether copolymer), Amoco's Ultradel™ (fluorinated polyimide) and Asahi's CYTOP™ (perfluorovinyl ether cyclopolymer) are fluoroplastics currently pursued for optical device manufacture. See, for example, Eldad, I.; Schacklette, L. "Advances in Polymer Integrated Optics," *IEEE J. Quantum* 10 *Electronics* **2000**, 6(1), 54.

The use of a perfluorocyclobutyl-based homopolymer in an optical waveguide has been disclosed. See Fishbeck, G.; Moosbuerger, R.; Kostrzewski, C.; Achen, A.; Petermann, K. *Electronic Letters* **1997**, 33(6), 518. Also, the use of various perfluorocyclobutane (PFCB) homopolymers has been disclosed for various electronics 15 and other applications. See for example, United States Patent No. 5,159,038; U.S. Patent No. 5,037,917 and related patents.

Several patents relate to optical devices and methods for constructing them. For example, United States Patent No. 5,850,498 is directed to low stress optical waveguides. United States Patent No. 6,210,867 B1 is directed to methods for 20 fabricating low loss optical devices using a photoresist coated on a linear optical layer by a spin coating method. The photoresist is dipped into a developer fluid and baked, thereby forming a photoresist pattern defining specific areas upon which a metal layer is deposited. A vacuum deposition method such as sputtering, electron beam or thermal evaporation may be employed to deposit a metal substrate.

25 A pending United States patent application (U.S.S.N. 09/604,748) which is commonly owned by the assignee of the present application, discloses optical fluoropolymers and methods of applying fluoropolymers in molding processes. The application is directed to the use of alternating perfluorocyclobutane and aryl ether linkages that are adapted for micromolding polymeric films by replicating a pattern or 30 image directly from a silicon master.

In the case of forming a polymer film using spin coating techniques, it is necessary to form a coating of sufficient thickness to manufacture a waveguide. Many

polymers cannot be dissolved at solids content when spin coated to manufacture a suitable waveguide thickness. In many instances, it requires multiple coats of polymer to achieve the necessary thickness, which introduces added interface problems, and can be costly and time consuming.

5 It has been recognized in the industry that a need exists for a suitable polymeric material and process that affords appropriate optical properties when applied in an optical device. A polymer and process of applying the polymer that is capable of achieving a suitably thick coating on the device is needed. A polymeric composition that is capable of maintaining a suitable solids thickness in solvent, thereby affording a
10 relatively thick coating, is desirable. A composition and method of application that employs a minimum amount of solvent, and a maximum solids content, is needed. Furthermore, polymeric compositions that exhibits low loss in the telecommunications wavelength and a compositionally controlled refractive index to match that of the silica optical fibers and other components would be desirable.

15 Summary of the Invention

A method and solution for making an optical device is provided in the invention of the application. The method may include steps of: providing a perfluorocyclobutyl-based copolymer composition, coating the perfluorocyclobutyl-based copolymer composition upon a substrate to form a first film, and thermally curing the first film to
20 form a thermoset film.

The invention comprises compositions that include fluoropolymers comprised of alternating perfluorocyclobutane and aryl ether linkages. These compositions possess the mechanical, thermal and structural properties and the desired optical clarity required for the manufacture of optical waveguides and the like. Chemical structures of some of
25 the compositions that may be employed in the invention of the application are shown in the attached drawings.

In some applications of the invention, the fluoropolymer may be used and as an optical signal carrier in a structural polymer matrix composite. Such composites may provide fully integrated high-speed data transmission mediums with switching and
30 routing capabilities. Thermoplastic and thermosetting polymers containing perfluorocyclobutane (PFCB) and arylene ether linkages provide high performance and a multi-functional polymer. PFCB segments may provide improved dielectric

insulation, optical clarity in the visible and near infrared wavelengths, increased solubility, melt processability, large thermo-optic coefficient ($-dn/dT$), low birefringence, and other valuable properties.

Of course, the above groups may be substituted with other alkyl or haloalkyl or
5 organic constituents on the one or more carbons, such as a carbon in the ring structure, and the above structures are provided by way of example and not by way of limitation. In some applications, a polymer is provided which is prepared from a trifluorovinyl aromatic ether (TVE). Trifluorovinyl aromatic ether monomer precursors are traditionally prepared in two high yielding steps from commercially available phenolic
10 precursors such as, for example, tris (hydroxyphenyl) ethane, biphenol, bis(hydroxyphenyl) fluorene, or other compounds. Partially inorganic monomers containing siloxane and phosphine oxide groups have also been synthesized using an intermediate strategy involving delivery of a TVE group intact via Grignard and organo-lithium chemistry.

15 Polymers with a wide range of mechanical, thermal and optical properties may be obtained using the above referenced chemistry. In particular, the refractive indices of the homopolymers or the co-polymers may be provided exactly as designed by careful regulation of monomer choice. Thus the refractive index at a given wavelength can be precisely controlled. The invention is capable of providing well defined
20 cyclopolymerization mechanisms using PFCB to prepare polymers with tunable thermal and optical properties. For example, random amorphous co-polymers with variable refractive indices, glass transition temperatures, and long term thermal stability above 350 degrees C. may be prepared by correct choice of a co-monomer composition. Co-polymers may be prepared by simple melt mixing of variable composition monomer
25 mixtures and heating under appropriate conditions. Using the invention, it is possible under some conditions to provide for precise control of refractive index by the choice of comonomer that is used. Thus, the thermal cyclopolymerization of aromatic trifluorovinyl ether monomers to perfluorocyclobutane polymers and co-polymers affords high temperature, low transmission loss, and variable refractive index for use in
30 optical devices.

In one aspect of the invention, optical devices and a process for fabricating optical devices may include an optical waveguide constructed of a core region and a clad

region. A lower clad layer is formed on a substrate with a refractive index that is less than that of the core regions.

In another aspect of the invention, a core and clad device structure is provided which exhibits a high thermo optic coefficient ($-dn/dT$) (refractive index change with temperature) for the manufacture of a thermo-optic switch.

Brief Description of the Drawings

A full and enabling disclosure of this invention, including the best mode shown to one of ordinary skill in the art, is set forth in this specification. The following Figures illustrate the invention:

Figure 1 shows the perfluorocyclobutane (PFCB) copolymer composition;

Figure 1A shows the structure of the copolymer that may be formed and used in the practice of the invention;

Figures 2A-2I depict various groups that may be substituted in a poly-aryl ether having perfluorocyclobutyl linkages as shown in Figure 1, wherein the Ar and/or Ar' groups would be substituted onto the linkage shown in Figure 1;

Figure 3 shows a spin coated thickness versus polymer concentration plot;

Figure 4 is a refractive index plot; and

Figure 5 shows a graph of a refractive index versus cure time curve.

Detailed Description of the Invention

Reference now will be made to the embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not as a limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in this invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents. Other objects, features and aspects of the present invention are disclosed in or are obvious from the following detailed description. It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention, which broader aspects are embodied in the exemplary

constructions.

Poly-aryl ethers containing perfluorocyclobutyl (PFCB) linkages are viable candidates for optical and opto-electronic applications due in part to their wide range of complementary properties. The properties of such compounds include excellent thermal and thermo-oxidative stability, high T_g , low moisture absorption, low dielectric constant, variable refractive index, and desirable melt and solution processability. Furthermore, poly-aryl ethers containing PFCB linkages are among the few known optical polymers to possess low attenuations in the technologically important 1,550 and 1,300 nm region. And can be precisely index matched to silica optical fibers and exhibit a high thermo-optic coefficient.

PFCB polymers are prepared from trifluorovinyl aromatic ether monomers via a free radical mediated thermal co-polymerization mechanism as illustrated in Figure 1. A representative example of some of the groups that may be included and used as the Ar and/or Ar' group as shown in Figure 1 are included in Figures 2A-2I.

A variety of monomers may be used to produce the PFCB polymers. Bis- and tris-functionalized TVE monomers polymerize to form linear or network polymers respectively with unique optical, thermal and mechanical properties. Furthermore, accurate control over the polymer properties may be achieved by co-polymerization.

It has been surprisingly discovered in the practice of the invention that compositions formed from structures as shown in Figures 1 and 2 may be advantageously used to provide high solids content solutions for coating on substrates in the construction of optical devices, and optical waveguides. High solids content solutions afford the opportunity to build relatively thick films upon the surface of a substrate, which is very desirable in the construction of such devices.

In the practice of one aspect of the invention, it is possible to copolymerize specific comonomers to provide variable and relatively thick core and clad copolymers for waveguide applications such as switches, modulators, attenuators, and the like. Alternatively, mixtures of homopolymer oligomers could be dissolved in a solvent to provide a similar solution, and then coated and cured. By thick, it is meant having a thickness of at least about 0.6 microns. In some applications, a thickness of 1 micron or more may be achieved in only one coat. In other preferred embodiments of the invention, a thickness of at least about 2 microns may be achieved. Thickness levels

from 2-10 microns also can be achieved, and in some aspects of the invention, it may be possible to achieve thickness levels well over 10 microns, up to and including at least about 50 microns in some particular embodiments of the invention.

The solution processability of the compositions in the practice of the invention is especially favorable. A reactive copolymer is provided which can be dissolved in very low amounts of solvent so that especially thick coatings can be prepared. The films are then thermally cured (i.e. advanced or polymerized) until they comprise three dimensional "network" polymer. The coatings then may be patterned by lithography or reactive ion etching ("RIE") or such as electron beam methods, or micromolding. In general, the network polymer formed is not soluble and will withstand other processing steps, which is another advantageous feature of the invention. The first layer structures may be coated more than once until a core/clad optical device is formed that is multilayered. High solids content of the copolymer solutions, and a suitable copolymer with appropriate properties, are necessary factors to consider in the practice of the invention.

Monomers shown in Figures 2A-2I may be used for optical applications. Bis and tris functionalized TVE monomers polymerize to form linear or network polymers respectively with unique optical, thermal and mechanical properties. Accurate control over polymer properties can be achieved by copolymerization. In addition, methods have been developed that preclude the need for elastomeric negative molds for more cost effective and reproducible prototypes, as further shown below.

PFCB polymers can be prepared neat or in solution at temperatures in excess of 160°C and do not require initiators or catalysts. The polymerization proceeds via a thermally activated cyclodimerization process. Although free-radical mediated, the cyclo-addition polymerization follows classical step growth kinetics. The polymers can be advanced to precisely controlled viscosity, molecular weight and dispersity by simple heating. The bifunctional TVE monomers yield linear polymers with M_n approaching 100,000 whereas trifunctional monomers can be melt advanced to branched pre-networks and processed prior to final cure. PFCB materials, in general, possess excellent thermal ($T_g=120-350$ °C), mechanical and environmental properties providing long-term stability at about 350 °C.

The step growth kinetics by which PFCB polymers are formed allows for easy

control of parameters important to coating technology. Monomer can be solution advanced at 150 degrees C. in typical solvents known in the art. A precisely controlled viscosity may be achieved, with correct molecular weight and polydispersity. The pre-polymer solution may be spin coated, dip coated, sprayed, or otherwise applied to the substrate by techniques employed in the art of optical device fabrication. Spin coating is known to provide high quality, defect free films. The film typically is cured by baking under nitrogen at temperatures ranging from about 235 degrees to about 325 degrees C. for several hours depending upon the application.

Solids content of solutions of PFCB copolymer employed may be from about 10% to about 70% films or plaques can be prepared by melt-mixing variable composition monomer mixtures and heating at 150-200 °C under an inert atmosphere.

One useful copolymer composition is made by polymerizing the species shown in Figures 2A and 2B (50 wt% compositions) which has been known to provide a measured $T_g = 220$ °C.

Copolymer solutions suitable for spin coating variable thick films may be prepared in mesitylene solution, yet other solvents such as N-methylpyrrolidinone and dimethylsulfoxide also can be used due to the wide ranging and excellent solubility exhibited by trifluorovinyl ether monomers and pre-network copolymer intermediates. For optical device fabrication, many copolymers studied to date contain the trifunctional monomer shown in Figure 2B so that the advanced intermediate is a branched copolymer of variable conversion and thus molecular weight and viscosity may be controlled prior to thermal cure to a cross-linked network.

For example, copolymer solutions in excess of 80 wt % polymer can be obtained (see Table1). This enables the preparation of thick films (on the order of 10 μ m) in one spin coat. The ability to spin coat very thick films is a unique feature for high performance PFCB polymers and thereby ensures a homogeneous layer in the final structure versus the multiple spin and cure cycles needed otherwise to achieve the desired thickness.

Figure 3 illustrates one spin curve for polymer solutions formed from copolymers utilizing the two monomer species shown in Figures 2A/2B, ranging from 10-70 weight percent solids at 600 rpm. The range can be tuned precisely with the expected change with spin rate.

Figure 4 illustrates the refractive index (@ 1550 & 653 nm) tunability for two example copolymers as a function of composition. As shown, a wide range of indices can be obtained through choice of composition.

5 Process parameters can be precisely controlled by choice of comonomer and polymerization time and temperature. After spin coating, the cyclopolymerization is continued by heating under inert atmosphere to the desired second glass transition temperature (T_g). Table 1 illustrates selected conditions and properties for PFCB copolymers targeted for optical applications.

TABLE 1

Condition or Property	Controlled Range
Copolymer solution concentration (mesitylene)	Up to 90 wt %
Single spin coat thickness	Up to 15 μ m
Copolymerization temperature / time	140-160 $^{\circ}$ C / 1 – 10 h
Weight average molecular weight (GPC)	(500 – 50,000)
Molecular weight distribution (GPC)	1.2 – 20 M_w/M_n
Solution viscosity (RMS)	0.02 – 100 Pa s
Cure temperature / time	120 – 350 $^{\circ}$ C / 0.1 – 3 h
Glass Transition Temperature (DSC T_g)	175 – 350 $^{\circ}$ C
Patterning Technique	Micromolding or RIE
Loss at 1550 nm	< 0.25 dB/cm
Refractive index at 1550 nm	1.449 – 1.508
Birefringence	< 0.01

10

The attenuation at 1550 nm for select copolymers is lower than that reported in the prior art which used homopolymers of monomer 2B in Fig. 2 instead of copolymers. That is, the use of the monomer in Figure 2B, is lower due to the decrease of aliphatic

groups contained only in that particular species (2B) and the intimate compatibility at the core / clad interface for waveguide structures made solely from PFCB copolymers.

The evolution and stability of optical properties is also of major concern for processing and performance of polymer integrated optics. The stability of the polymer's optical properties over time and during multiple heat and cool cycles is currently a significant issue. Initial results using polymers of the invention are shown in Figure 5 where the refractive index is plotted as a function of cure time at 200 °C for the monomer of Figure 2B. As shown, the refractive index changes dramatically during cure yet quickly stabilizes in less than 2 hours. Further, the refractive index is completely stable after multiple heat cure cycles and continued heating at 200 °C.

The copolymers of the invention exhibit relatively low loss in the telecommunications wavelength at which they are employed. That is, a low optical loss is observed at about 1550 nm. Loss levels of less than about 0.3, and sometimes less than about 0.1 dB/cm, may be achieved using the compositions and or more, with greater thickness film layers being achieved using greater solids content percentages. Solvents used may be any of the commonly known solvents, including for example, mesitylene. Spin coating is performed by either pouring the solution (less than 10 ml) upon a static silicon wafer (secured by vacuum on the spin coater chuck) and spinning at the desired speed and time (electronically controlled), or pouring the solution on the spinning wagger.

General Procedure Experimental Details

Monomers were prepared from their corresponding phenolic precursors. ¹H NMR data were obtained on a Bruker AC-300 spectrometer. ¹⁹F NMR 188 MHz data were obtained on a Bruker AC-200 spectrometer. Functional group (TVE) conversion data (Table 2) was determined by integration of the TVE fluorine signals and PFCB fluorine signals. Chloroform-*d* was used as solvent, and chemical shifts reported are internally referenced to tetramethylsilane (0 ppm), CDCl₃ (77 ppm), and CFCl₃ (0 ppm) for ¹H, ¹³C, and ¹⁹F nuclei, respectively. Infrared analyses were performed on neat oils or free standing films using a Nicolet 550 Magna FTIR spectrophotometer. IR data used for polymerization kinetics was obtained in reflectance mode on an ASI React IR System. Gas chromatography/mass spectrometry (GC/MS) data were obtained from a Varian Saturn GC/MS. Gel permeation chromatography (GPC) data were collected in THF using a

Waters 2690 Alliance System with refractive index detection at 35 °C, and equipped with two consecutive Polymer Labs PLGel 5mm Mixed-D and Mixed-E columns. Retention times were calibrated against Polymer Labs Easical PS-2 polystyrene standards. The copolymer solution viscosity was measured with a TA AR1000-N Rheometer. A Geometry of cone-plate was used with a diameter of 40 mm, the 2 degree angle and 43 μ m truncation. The frequency dependence of viscosity was measured within the frequency range of 3.0 to 300.0 rad/s at room temperature. The viscosity data reported here is read at the shear rate of 100.0 rad/s. DSC data were obtained from a Mettler-Toledo 820 System under a nitrogen atmosphere at a scan-rate of 10°C/min.

Table 2 Selected Copolymer Data

Ex.	Monomer (g)	Monomer (g)	wt.% polymer in mesitylene	Polym. time (h) at 150/160 °C	Mn	Mw	Mw/Mn	Olefin conv. (%)	Viscosity (Pa.s)	*Refractive index @1550 nm	*Glass Transition, T _g (°C)
1	2B(175)	0	75	1.45	2444	7033	2.89	34.8	0.1	1.4883	350
2	2B(40)	2A(40)	80	2.5	589	1212	2.06	37.3	0.133	1.5036	225
3	2B(17.38)	2C(7.78)	50	8	1859	4656	2.5	44.2	6.8	1.4785	221
4	2B(17.38)	2C(7.78)	75	5	3943	9709	2.45	52.2	1.575	1.4801	220
5	2B(50)	2A(50)	70	2.15	661	1178	1.78	37	1.1	1.5008	224
6	2B(160)	2A(40)	75	3.2	2508	4846	1.93	40	0.1	1.4892	285
7	2B(80)	2A(20)	70	1.45	899	2008	2.34	32	0.085	1.4892	286

*After cure at 200 °C for 2 h.

Copolymer solutions were prepared by dissolving one or more monomers as shown in Figs. 2A-2B (50-80 wt %) in freshly distilled and filtered mesitylene (5 L flask, ca. 3 L polymer solution). The solution was stirred mechanically and degassed for 30 minutes with a dry nitrogen spurge. The spurge was stopped and a positive pressure of nitrogen was applied and the reaction flask was heated to 150 °C and stirred for several hours to form the copolymers.

The copolymer films were applied to silicon wafers using a KW-4A Spincoater (Chemat Technology, Inc.) using standard spin coating techniques. Filtered polymer solutions were coated from 600 to 2000 rpm for about 60 seconds, and then cured in an oven 200 °C under nitrogen for 2 hours. Alternatively, films could be hot plate cured under nitrogen, in other applications of the invention. Also, the temperature could potentially be increased, or decreased, depending upon the particular application and copolymer employed.

Film thickness was measured by a profilometer, Alphastep 200, which is

manufactured by Tencor Company. Refractive index data was obtained from a Metricon Model 2010 Prism Coupler System from Metricon Company. Birefringence was calculated as the difference between the TE mode and the TM mode ($\eta_{TE} - \eta_{TM}$). Absorption spectra were measured using a Perkin Elmer Lambda 900 UV/Vis/NIR spectrophotometer. Spectra were taken over the wavelength range 3200-200 nm at a scan rate of 120 nm/minute.

Example 1: Homopolymer of 2B (75 wt% in mesitylene)

To a three neck round bottom flask equipped with nitrogen inlet, reflux condenser and mechanical stir was added 175 g of pure monomer **2B** and 58.3 g of filtered mesitylene. The solution was degassed as described in the general procedures and experimental details above. The clear solution was then heated to 150-160 °C for 1.45 h and allowed to cool. The resulting homopolymer exhibited a olefin conversion of 34.8 %, a number average molecular weight (Mn) of 2,444 and a weight average molecular weight (Mw) of 7033, and a molecular weight distribution of 2.89 (See Table 2). The polymer solution was spin coated and cured as described above and gave a thermoset film with refractive index of 1.4883 (at 1550 nm) and a glass transition temperature of 350 °C.

Example 2: Copolymer of 2B and 2A (50:50 ratio, 80 wt% in mesitylene)

To a three neck round bottom flask equipped with nitrogen inlet, reflux condenser and mechanical stir was added 40 g of pure monomer **2B**, 40 g of pure monomer **2A**, and 10 g of filtered mesitylene. The solution was degassed as described in the general procedures and experimental details above. The clear solution was then heated to 150-160 °C for 2.5 h and allowed to cool. The resulting copolymer exhibited a olefin conversion of 37.3 %, a number average molecular weight (Mn) of 589 and a weight average molecular weight (Mw) of 1212, and a molecular weight distribution of 2.06 (See Table 2). The polymer solution was spin coated and cured as described above and gave a thermoset film with refractive index of 1.5036 (at 1550 nm) and a glass transition temperature of 225 °C.

Example 3: Copolymer of 2B and 2C (70:30 ratio, 50 wt% in mesitylene)

To a three neck round bottom flask equipped with nitrogen inlet, reflux condenser and mechanical stir was added 17.4 g of pure monomer **2B**, 7.8 g of pure monomer **2C**, and

25 g of filtered mesitylene. The solution was degassed as described in the general procedures and experimental details above. The clear solution was then heated to 150-160 °C for 8 h and allowed to cool. The resulting copolymer exhibited a olefin conversion of 44.2 %, a number average molecular weight (Mn) of 1859 and a weight average molecular weight (Mw) of 4656, and a molecular weight distribution of 2.5 (See Table 2). The polymer solution was spin coated and cured as described above and gave a thermoset film with refractive index of 1.4785 (at 1550 nm) and a glass transition temperature of 221 °C.

Example 4: Copolymer of 2B and 2C (70:30 ratio, 75 wt% in mesitylene)

To a three neck round bottom flask equipped with nitrogen inlet, reflux condenser and mechanical stir was added 17.4 g of pure monomer 2B, 7.8 g of pure monomer 2C, and 8 g of filtered mesitylene. The solution was degassed as described in the general procedures and experimental details above. The clear solution was then heated to 150-160 °C for 5 h and allowed to cool. The resulting copolymer exhibited a olefin conversion of 52.2 %, a number average molecular weight (Mn) of 3943 and a weight average molecular weight (Mw) of 9709, and a molecular weight distribution of 2.45 (See Table 2). The polymer solution was spin coated and cured as described above and gave a thermoset film with refractive index of 1.4801 (at 1550 nm) and a glass transition temperature of 220 °C.

Example 5: Copolymer of 2B and 2A (50:50 ratio, 70 wt% in mesitylene)

To a three neck round bottom flask equipped with nitrogen inlet, reflux condenser and mechanical stir was added 50 g of pure monomer 2B, 50 g of pure monomer 2A, and 43 g of filtered mesitylene. The solution was degassed as described in the general procedures and experimental details above. The clear solution was then heated to 150-160 °C for 2.15 h and allowed to cool. The resulting copolymer exhibited a olefin conversion of 37 %, a number average molecular weight (Mn) of 661 and a weight average molecular weight (Mw) of 1178, and a molecular weight distribution of 1.78 (See Table 2). The polymer solution was spin coated and cured as described above and gave a thermoset film with refractive index of 1.5008 (at 1550 nm) and a glass transition temperature of 224 °C.

Example 6: Copolymer of 2B and 2A (80:20 ratio, 75 wt% in mesitylene)

To a three neck round bottom flask equipped with nitrogen inlet, reflux condenser and mechanical stir was added 160 g of pure monomer 2B, 40 g of pure monomer 2A, and

67 g of filtered mesitylene. The solution was degassed as described in the general procedures and experimental details above. The clear solution was then heated to 150-160 °C for 3.2 h and allowed to cool. The resulting copolymer exhibited a olefin conversion of 40 %, a number average molecular weight (Mn) of 2508 and a weight average molecular weight (Mw) of 4846, and a molecular weight distribution of 1.93 (See Table 2). The polymer solution was spin coated and cured as described above and gave a thermoset film with refractive index of 1.4892 (at 1550 nm) and a glass transition temperature of 285 °C.

Example 7: Copolymer of 2B and 2A (80:20 ratio, 70 wt% in mesitylene)

To a three neck round bottom flask equipped with nitrogen inlet, reflux condenser and mechanical stir was added 80 g of pure monomer 2B, 40 g of pure monomer 2A, and 20 g of filtered mesitylene. The solution was degassed as described in the general procedures and experimental details above. The clear solution was then heated to 150-160 °C for 1.45 h and allowed to cool. The resulting copolymer exhibited a olefin conversion of 32 %, a number average molecular weight (Mn) of 899 and a weight average molecular weight (Mw) of 2008, and a molecular weight distribution of 2.34 (See Table 2). The polymer solution was spin coated and cured as described above and gave a thermoset film with refractive index of 1.4892 (at 1550 nm) and a glass transition temperature of 286 °C.

Other solvents besides mesitylene could be used in the practice of the invention, such as other high boiling hydrocarbons, N-methylpyrrolidinone, dimethylsulfoxide, and others. For optical device fabrication, most copolymer intermediates enable molecular weight and viscosity control prior to thermal cure to a cross-linked network.

It is understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention, which broader aspects are embodied in the exemplary constructions. The species shown in Figures 2A-2I could be employed in numerous different combinations in the practice of the invention, at various ratios and the like. The invention is shown by example in the appended claims.

What is claimed is:

1. A method of making an optical device, comprising:
 - (a) providing a copolymer composition of the structural formula:
wherein z is greater than or equal to 2, and
 - 5 wherein x and y each are greater than or equal to 1, respectively, and
wherein the Ar and the Ar' groups each comprise substituted or nonsubstituted aryls selected from the group comprising:
 - (b) applying the copolymer composition by coating to form a film.
2. The method of claim 1 in which the copolymer is prepared from a trifluorovinyl aromatic ether.
3. The method of claim 1 in which the copolymer composition is spin coated.
4. The method of claim 1 in which the copolymer composition is coated by dipping.
5. The method of claim 1 in which the copolymer composition is dissolved in a solvent prior to coating the copolymer composition.
6. The method of claim 1 comprising the additional step of:
 - (c) thermally curing the film to form a cured thermoset film.
7. The method of claim 6 in which the thickness of the thermoset film is at least about 0.6 microns.
8. The method of claim 6 in which the thickness of the thermoset film is at least about 0.8 microns.

9. The method of claim 6 in which the thickness of the thermoset film is at least about 0.9 microns.

10. The method of claim 6 in which the thickness of the thermoset film is at least about 1 micron.

11. The method of claim 6 in which the thickness of the thermoset film is at least about 2 microns.

12. The method of claim 6 in which the thickness of the thermoset film is at least about 3 microns.

13. The method of claim 6 in which the thickness of the thermoset film is at least about 4 microns.

14. The method of claim 6 in which the thickness of the thermoset film is at least about 5 microns.

15. The method of claim 6 in which the thickness of the thermoset film is at least about 10 microns.

16. A method of making an optical device, comprising:

- (a) providing a perfluorocyclobutyl-based copolymer composition,
- (b) coating the perfluorocyclobutyl-based copolymer composition upon a substrate to form a first film, and
- (c) thermally curing the first film to form a thermoset film.

17. The method of claim 16 in which the thermoset film comprises a

substantially transparent polymeric core.

18. The method of claim 17 comprising the additional step of:
(d) applying cladding to the outer surface of the core to form an optical waveguide.

19. The method of claim 16 in which the coating step is accomplished by spin coating.

20. The method of claim 16 in which the perfluorocyclobutyl-based copolymer composition is applied to the substrate in a solution having at least about 25% solids by weight.

21. The method of claim 16 in which the perfluorocyclobutyl-based copolymer composition is applied to the substrate in a solution having at least about 40% solids by weight.

22. The method of claim 16 in which the perfluorocyclobutyl-based copolymer composition is applied to the substrate in a solution having at least about 60% solids by weight.

23. The method of claim 16 in which the perfluorocyclobutyl-based copolymer composition is applied to the substrate in a solution having at least about 70% solids by weight.

24. The method of claim 16 in which the cured film comprises a thickness of at least about 1 micron.

25. The method of claim 16 in which the cured film comprises a

thickness of at least about 2 microns.

26. The method of claim 16 in which the cured film comprises a thickness of at least about 3 microns.

27. The method of claim 16 the film is formed from a coating comprised from a mixture of perfluorocyclobutyl based homopolymers.

28. A method of making an optical device, comprising:

- (a) providing a perfluorocyclobutyl-based copolymer composition,
- (b) spin coating the perfluorocyclobutyl-based copolymer composition upon a substrate to form a first film, and
- 5 (c) thermally curing the first film to form a cured film having a thickness of at least about 2 micron.

29. An optical device constructed by the method of:

- (a) providing a perfluorocyclobutyl-based copolymer composition having a solids content of at least about 50%,
- 5 (b) spin coating the perfluorocyclobutyl-based copolymer composition upon a substrate to form a first film, and
- (c) thermally curing the first film to form an optical device, thereby forming an optical device having a cured film thickness of at least about 0.6 microns.

30. A solution for making an optical device in which the solution comprises a perfluorocyclobutyl-based copolymer.

31. The solution of claim 30 in which the solution is composed of a mixture of perfluorocyclobutyl-based homopolymers.

32. The solution of claim 30 in which the solution comprises a mixture of at least two different perfluorocyclobutyl-based copolymers.

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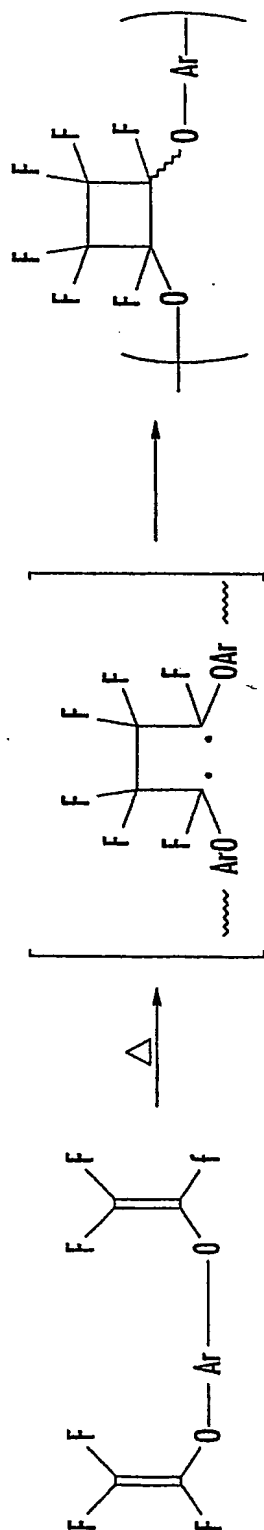


FIG. 1.

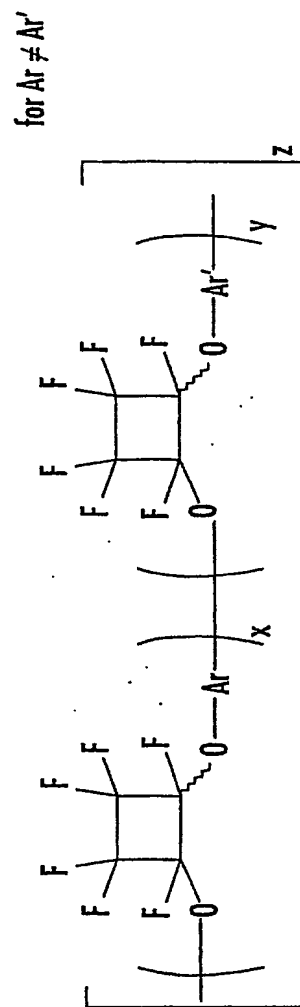
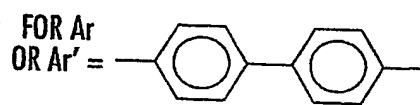


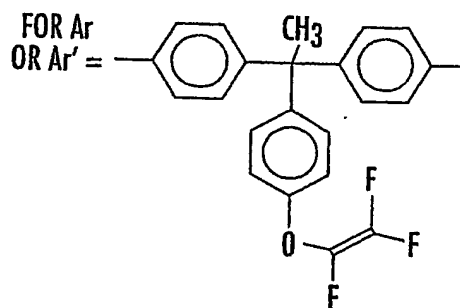
FIG. 1A.

2/6



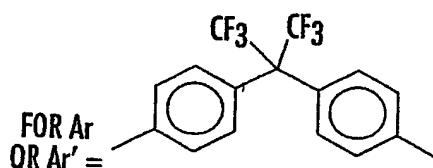
$T_g = 165\text{ }^{\circ}\text{C}$

FIG. 2A.



$T_g = 350\text{ }^{\circ}\text{C}$

FIG. 2B.



$T_g = 120\text{ }^{\circ}\text{C}$

FIG. 2C.

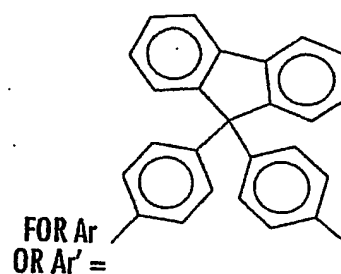


FIG. 2D.

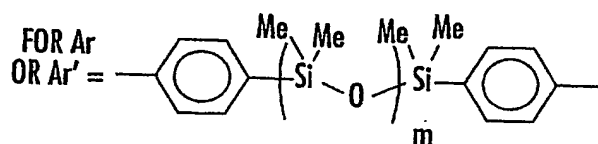


FIG. 2F.

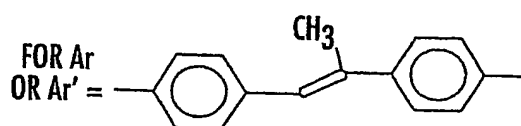
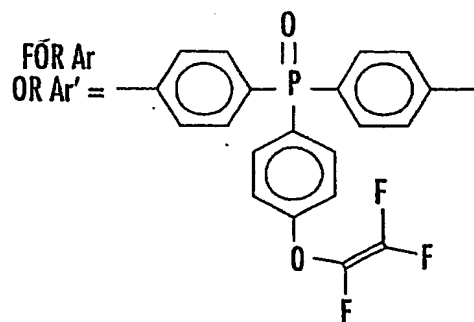
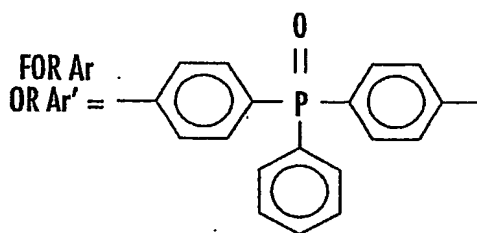
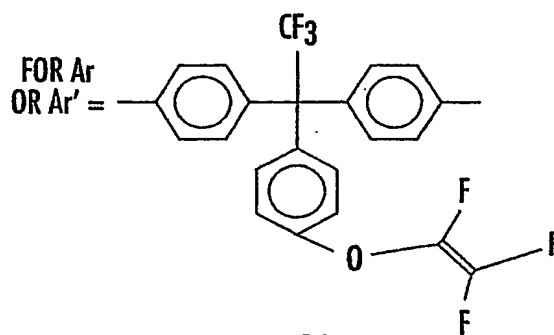
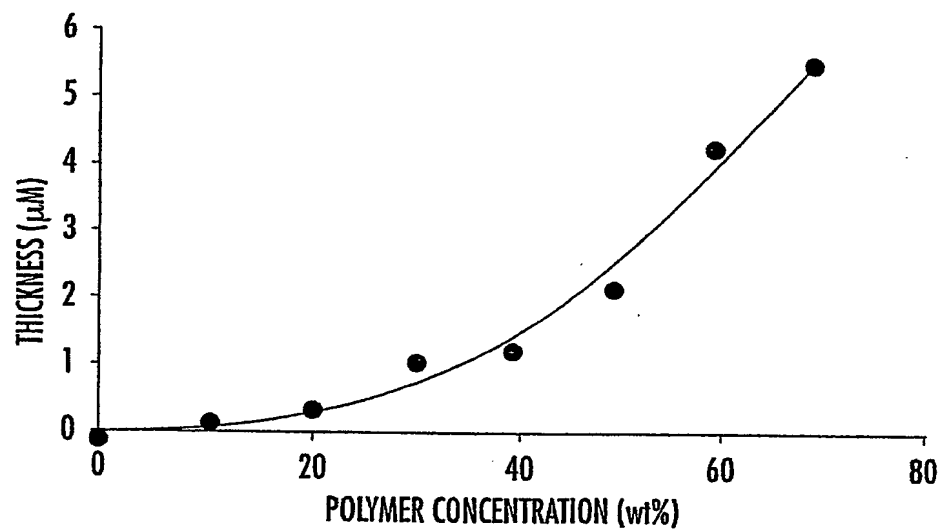


FIG. 2E.

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*FIG. 2G.**FIG. 2H.**FIG. 2I.*

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SPIN COATED FILM THICKNESS AT 600-RPM VS. WT.% COPOLYMER IN MESITYLENE FOR
COPOLYMER OF SPECIES OF FIGURE 2A/2B

FIG. 3.

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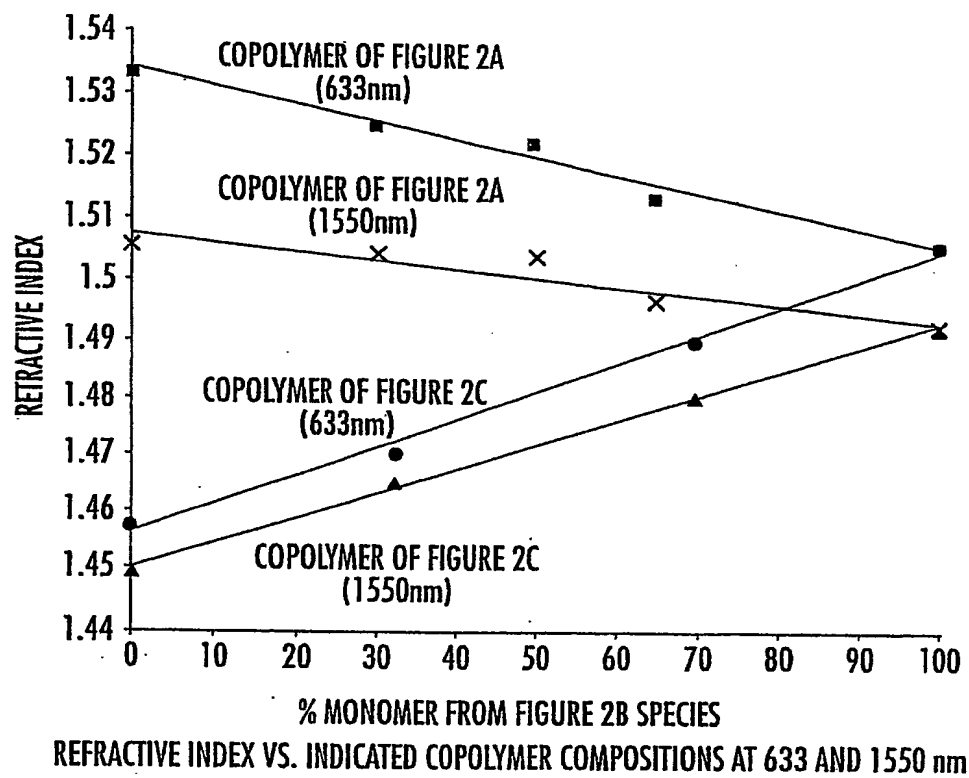
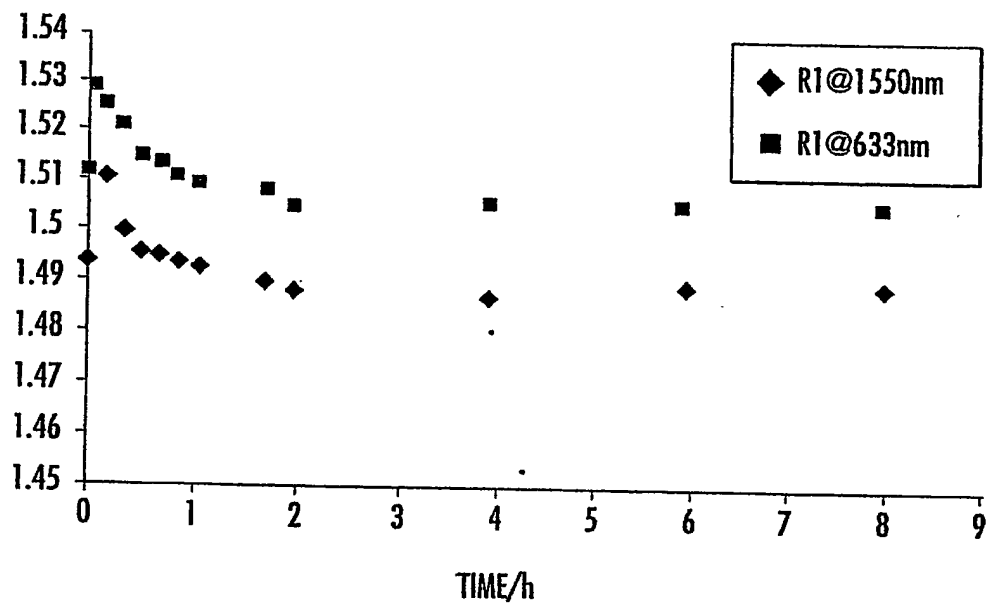


FIG. 4.

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REFRACTIVE INDEX VS. CURE TIME AT 200°C FOR THE MONOMER OF FIGURE 2B

FIG. 5.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/19920

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : G02B 6/10; C08F 12/20, 14/18, 8/00
 US CL : 430/321; 385/143, 130, 131; 526/247,334

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 430/321; 385/143, 130, 131; 526/247,334

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 CAS and WEST (copolymer? or terpolymer?) and (PFCB or perfluorocyclobut?)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	SHAH, H. et al., "Perfluorocyclobutane (PFCB) polymers for Optical Fibers and Dielectric waveguides", Polymer Preprints, Vol. 40(2) pp. 1293-1294 (1999), figure 3, table 1 and page 1293	30-32 ----- 1-3,5,6,16,17,19-21;27 and 30-32
X	HOEGLUND, A.B., et al., "Random Perfluorocyclobutyl Copolymers with Controlled Optical Properties", Polymer Preprints, Vol 41(2) pp. 1163-1164 (08/2000), see figures 2 and 4.	30-32
X --- Y	SMITH, D.W., et al., "Perfluorocyclobutane (PFCB) Polyaryl Ethers: Versatile Coatings Materials", J. Fluorine Chem., vol. 104(1) pp. 109-117 (5/19/2000), see figures 4-6 and pages 110 and 112.	30-32 ----- 1-32
Y	FISCHBECK, G., et al., "Singlemode Optical Waveguides Using a High Temperature Stable Polymer with Low Losses in the 1.55 micron Range", Electron. Lett., Vol.; 33(6) pp. 518-519 (03/1997), see page 518, left column.	1-32

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

27 September 2002 (27.09.2002)

Date of mailing of the international search report

05 NOV 2002

Name and mailing address of the ISA/US

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C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---	US 5,426,164 A (BABB et al.) 20 June 1995 (20.06.1995), example 2 and columns 19/lines 7-19 and column 3 at lines 3-7.	30-32
Y		1-32
X ---	US 5,159,038 A (BABB et al.) 27 October 1992 (27.10.1992) examples 10 and 11.	30-32
Y		1-32
Y	US 5,850,498 A (SHACKLETTE et al.) 15 December 1998 (15.12.1998) see figures 1, 1a and column 13 at line 10	18
Y	US 5,246,782 A (KENNEDY et al.) 21 September 1993 (21.09.1993), column 15/lines 9-55 and table 5 in column 36	1-32